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MOTOR GASOLINE

PROPERTIES, LABORATORY METHODS OF TESTING, AND PRACTICAL SPECIFICATIONS

BY

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MOTOR GASOLINE; PROPERTIES, LABORATORY METHODS OF TESTING, AND PRACTICAL SPECIFICATIONS.

By E. W. Dean.

INTRODUCTION.

One of the most desirable conditions to be attained in the development of technical or commercial undertakings is that producers and users shall be able to determine the relative desirability of commodities on the basis of simple and accurate tests. Such a condition has not yet been reached in regard to petroleum, and many persons believe that satisfactory specifications for the purchase of petroleum and its products can not be prepared on the basis of laboratory tests. Claims are frequently made that the only adequate test for gasoline or any other petroleum product is that of actual use.

Such claims, it is hoped, may soon be proved extreme and untenable, but the fact remains that the drawing of specifications for the purchase and sale of petroleum products has not yet been accomplished with any great degree of satisfaction. The present paper is not published as a last word on even one phase of the subject, but is intended to aid the public in becoming generally acquainted with methods of testing gasoline, in the hope that a sufficiently wide application of the principles set forth will result in perfecting specifications as satisfactory as those used in transactions involving many other commodities.

During the spring of 1916, the Bureau of Mines began to collect information regarding specifications then employed for petroleum products. From replies to letters written to various agencies it learned that few if any purchasers had satisfactory standards for these commodities, and especially for gasoline. In the few attempts made to define the quality of motor fuel, many of the specifications were either inadequate or unreasonable.

Specific gravity is the property by which gasolines have been most generally differentiated, but under present conditions a specific gravity determination is entirely inadequate; it may give a high rating to a poor gasoline and a low rating to a good one. More adequate testing methods are now being employed, but these are not

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always satisfactory and are not thoroughly understood. The general tendency has been either to specify tests that are unreliable or else to make requirements unreasonably severe. Many buyers still believe that only "straight" refinery gasolines, free from casinghead and cracked products, are desirable, and the tests they require discriminate against a large part of the present market supply of gasoline.

The analytical methods used for testing gasoline are of fairly recent development and the published descriptions of them are not found in standard textbooks. Some of the methods are decidedly unsatisfactory, having been devised to meet immediate needs when time did not permit thorough study of the factors involved. These methods meet tolerably well the needs of refiners who possess information regarding the sources of raw material and the method of production, but they do not suffice for the chemist who is given a sample of gasoline and requested to make a comprehensive statement of its properties. Some of the tests in use are not standardized, and there are substantial differences in the methods of conducting them in various laboratories.

Also there is a lack of knowledge regarding the practical interpretation of the results obtained in the laboratory, the general tendency being to overemphasize the importance of some particular figure. Specific gravity formerly was considered a complete index of the properties of a gasoline. At present there is danger that overemphasis may be placed on some other equally unimportant factor. One of the chief objects of this paper is to indicate rational methods of interpreting analytical results.

ACKNOWLEDGMENTS.

The Bureau of Mines began its study of gasoline specifications at the suggestion of W. A. Williams, formerly chief petroleum technologist of the bureau. A large part of the work was conducted under the active supervision of Mr. Williams and much credit is due him for assistance and advice.

To Van. H. Manning, director of the bureau, who has shown particular interest in the problem, credit is due for guidance in the assembling of a large part of the material presented.

Dr. C. W. Waidner and his colleagues of the gasoline committee of the Bureau of Standards furnished valuable criticism and advice with regard to the presentation of material included in the present paper.

W. A. Jacobs and C. R. Bopp, of the petroleum division of the Bureau of Mines, obtained important information through the collection and analysis of samples of the various gasolines now being marketed.

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The Bureau of Mines is indebted to the men and organizations that have supplied valuable constructive criticism of preliminary drafts of the present paper. The information presented is in large part based on the data thus obtained, and the hearty cooperation of refiners, engineers, and manufacturers is cordially acknowledged.

IMMEDIATE NEED OF GASOLINE SPECIFICATIONS.

Various considerations led the Bureau of Mines, in its study of specifications for petroleum and petroleum products, to take up first the problem of specifications for gasoline. The General Supply Committee of the Federal Government in the District of Columbia requested the Bureau of Mines to assist in formulating specifications for purchases of motor fuel. Also, in different parts of the country a demand has arisen for the local adoption of gasoline regulations, and the bureau has deemed it advisable to publish information that may help to prevent useless or troublesome legislation.

The reader should remember that the Bureau of Mines has no authority and no desire to assume the police power exercised by States and municipalities. Its work is investigative, and it endeavors to act in an educational and advisory capacity. Hence its aim in publishing this paper is to present information on desirable properties and methods of testing.

Of course, no hard and fast line differentiates good gasoline from bad. Actually standards of quality seem to be varying with advances in engine design, so that what was once decidedly poor gasoline can now be successfully used. Probably the limit of change has not been reached yet; and the writer has taken care to point out that the grades of gasoline now on the market do not necessarily represent future grades.

DESIRABLE PROPERTIES OF GASOLINE.

The essentially desirable properties of gasoline may be summarized briefly as follows:

(1) The gasoline should not contain too large a percentage of highly volatile products, which tend to cause large evaporation losses and excessive danger in handling and storage, but should have sufficient volatile constituents to permit starting an engine under reasonably unfavorable conditions without preheating.

(2) The gasoline should not contain any considerable percentages of heavy or nonvolatile constituents, which after atomization into the engine cylinders can not be completely vaporized and burned.

(3) The gasoline should not contain a material which after combustion leaves a residue that collects in the motor.

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(4) The gasoline should be free from substances that attack metal, either before or after combustion. Unremoved acid (used in refining) falls under this head.

(5) Neither the gasoline nor its products of combustion should have a strong or markedly disagreeable odor, because of this being objectionable to users of automobiles.

(6) The gasoline should be free from noncombustible material, such as water, sediment, acid, etc.

These stated requirements are simple in principle and are almost axiomatic. The chief problem is to fix limits, defined by actual tests, that will satisfy the desirable conditions.

TYPES OF GASOLINE MARKETED AND THEIR GENERAL PROPERTIES.

There are at present on the market types of gasoline produced by several general methods. These may be classified as follows:

1. "Straight" refinery gasoline.
2. Blended casing-head gasoline.
3. Cracked and blended gasoline.

"STRAIGHT" REFINERY GASOLINE.

"Straight" refinery gasolines are produced by methods that vary somewhat in different parts of the country but in general are similar. Crude oil is distilled in a fire still and a cut made when the gravity of the product reaches some predetermined mark. So-called crude naphtha, or benzine, is acid refined and steam distilled. Several products of different ranges of volatility may be produced, or the steam distillation may simply separate the product from the less volatile bottoms, which go into the burning oil stock.

"Straight" refinery gasolines are generally characterized by a low content of unsaturated and aromatic hydrocarbons, and by a distillation range free from marked irregularities.

BLENDED CASING-HEAD GASOLINES.

During the past few years so-called casing-head gasoline, obtained from natural gas by compression or absorption, has come on the market. "Straight" casing-head gasoline is too volatile for general use and, before being marketed, is generally blended with enough heavy naphtha to produce a mixture that can be used safely and is moderately cheap. In general, blended casing-head gasoline is characterized by a volatility range that shows a considerable percentage of constituents of low and of high boiling points, but a lack of intermediate products. Frequently, however, the blending is done

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in a manner difficult to detect, the natural-gas gasoline being used in moderately small proportion with "heavy" straight-run naphtha in order to make a product having a desirable percentage of volatile constituents.

As regards its chemical properties, blended casing-head gasoline seems to be identical with the "straight" refinery products of the same distillation range. Characteristic physical properties of blended gasolines are due wholly to the details of blending.

CRACKED OR SYNTHETIC GASOLINES.

Important factors in the present supply of gasoline on the market are the cracked or synthetic gasolines. These are being marketed in enormous quantities, largely, if not altogether, in the form of blends with "straight" refinery and casing-head gasoline.

Cracked gasolines are similar to "straight" refinery products in most physical and chemical properties, but differ chemically in containing varying percentages of unsaturated and aromatic hydrocarbons. It has been demonstrated that these constituents, if present in moderate proportion, do not decrease the value of a gasoline. Also, competent authorities generally concede that by proper engine equipment and adjustment it is possible to use unsaturated hydrocarbons in practically unlimited proportion, although extensive experimental proof of this latter point does not seem to be available as yet.

PROPERTIES OF GASOLINE AND METHODS OF TESTING.

Before outlining a system of analyses and specifications, it seems desirable to discuss thoroughly the individual properties that might be considered important and also to consider analytical methods. This paper is not intended as a complete review of gasoline analysis, and those properties that are considered of minor practical importance are not discussed in detail.

COLOR.

Color is of some importance because it serves as an index of other qualities. Properly refined gasolines are water white and hence it seems desirable to include a color requirement in specifications for gasoline. It does not, however, seem necessary to employ a test involving any sort of a tintometer, as the rough-and-ready method of looking through the bottom of a 4-ounce sample bottle is adequate.

ODOR.

Gasoline should be free from rank and disagreeable odors, as these cause discomfort of users, especially if the odor has a tendency to

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cling to clothing. It is, of course, impossible to fix any definite standard for odor as to either quality or strength. The older requirements demanded the sweet, pleasant odor characteristic of high-test uncracked distillates. With the present necessity of using cracked gasoline this requirement has become impossible and the requirement of odor must be left in rather indefinite form.

WATER, SEDIMENT, AND OTHER FOREIGN MATTER.

Gasoline should obviously be free from water and other foreign matter. Water is seldom present in gasoline and is always easy to detect, as the two liquids are mutually insoluble.

ACIDITY.

Obviously, too, gasoline should not contain any acid from the refining process. This, however, seems to be a failing from which market products are largely free. Acidity may be detected by shaking a sample of the suspected gasoline thoroughly with a small quantity of water and testing the water with blue litmus paper.

CALORIFIC POWER, OR HEATING VALUE.

No data are at hand to show the effects of calorific power on the usefulness of a gasoline. However, the actual variations in calorific power for different kinds of gasoline seem to be relatively small, and as the mechanical energy developed in the engine is only a fraction of the heat produced these variations may be regarded as negligible. Some recent experiments[a] have shown that gasolines of widely differing physical properties varied only by a maximum of 2 per cent in calorific value per unit weight.

CONTENT OF AROMATIC HYDROCARBONS—BENZOL, TOLUOL, AND OTHERS.

At present little heed need be given to the effect of aromatic hydrocarbons in motor fuel, as these products are in tremendous demand for the manufacture of explosives, dyestuffs, and drugs. After the end of the war in Europe it may become necessary to devise a specification clause limiting the percentage of these hydrocarbons that a gasoline may contain, but it is equally possible that such action may be unnecessary, for present indications are that aromatic hydrocarbons are just as good motor fuel as nonaromatic. If limitation should become necessary it can probably be made most effectively and simply

[a] Rittman, W. F., Jacobs, W. A., and Dean, E. W., Physical and chemical properties of gasoline sold throughout the United States during the calendar year 1915; Technical Paper 163, Bureau of Mines, 1916, 45 pp.

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through the specific-gravity requirements. Aromatic hydrocarbons—benzol, toluol, and the others—have specific gravities of about 0.87 to 0.88 (29° to 30° B.) and boil at the same temperatures as nonaromatics having specific gravities between 0.70 and 0.76 (54° to 70° B.). For the present, however, there seems little need of considering the content of aromatic hydrocarbons.

UNSATURATED HYDROCARBONS.

The effect of unsaturated hydrocarbons on the properties of gasoline is another matter that has not been worked out completely. As already stated, there is conclusive evidence showing that gasolines containing moderate percentages of unsaturated hydrocarbons can be used with entire satisfaction, but it is not yet definitely established that the presence of unlimited proportions of these constituents causes no disadvantage.

In view of present market conditions it does not seem desirable to emphasize any requirements that may interfere with the development of cracking processes, as this now seems to offer the greatest possibility of conserving the country's petroleum resources.

The Bureau of Mines is preparing to publish the results of a study of the comparative advantages of various analytical methods of determining degrees of unsaturation. This study has shown that the acid-heat test, largely used by refiners, is little better than qualitative, and determination of iodine absorption by the Hanus method, though accurate and fairly rapid, requires some little skill of manipulation on the part of the operator. If experimental details are properly regulated, the measurement of the percentage absorbed by ordinary sulphuric acid seems on the whole the most desirable method.

SPECIFIC GRAVITY.

Specific gravity in itself is of very slight significance in determining the properties of gasoline. It may serve as an index of other properties, particularly volatility, if knowledge is at hand regarding the source and method of production of a gasoline. The determination of gravity has been and probably always will be one of the most useful tests that the refiner employs, but it is of but little value to the analyst who does not possess sufficient additional information to make proper interpretation of gravity results.

Methods of determining gravity are too well known to need discussion. The type of instrument chosen may be hydrometer, displacement balance (such as the Westphal), or a suitable pycnometer, according to the quantity of gasoline to be tested. Of these instruments the hydrometer is most convenient, the pycnometer least con-

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venient. The accuracy of the determination should be within 0.1 to 0.2 per cent. Gravity is generally expressed as the ratio of the densities of oil and water at the temperature of 60° F.

VOLATILITY.

Volatility is the basic property that determines the grade and usefulness of a gasoline. Unfortunately its influence is not simple enough for adequate discussion in a few words, chiefly because the advantages and disadvantages of various characteristics of volatility are so balanced that no one characteristic can be said to be either entirely desirable or entirely undesirable. For example, the presence of considerable percentages of low-boiling constituents in gasoline would seem desirable in that they permit easy starting of a cold engine. Against this advantage are the high prices of such gasolines and the considerable evaporation losses, the latter tending to increase danger in storage and handling.

General consideration of the numerous factors involved has led to the following conclusions regarding the desirable characteristics of the volatility of motor gasoline.

Gasoline should contain a moderate but not excessive proportion of low-boiling constituents, enough to permit easy starting of a cold engine but not enough to make evaporation losses excessive.

Gasoline should have a total volatility range wide enough to include constituents that have a high, but not too high, boiling point. For economic reasons affecting both the individual user and the country as a whole, this volatility range should be such that the gasoline contains the largest possible percentage of the original crude oil. It should not, however, be wide enough to exceed the limits of the vaporizing power of the automobile engine.

These two factors are not the only ones involved in the problem of volatility limits; but if properly attended to they generally take care of other essential features, such as "flexibility," freedom from carbon deposition, and development of maximum power.

Discussing the essential properties of gasoline is relatively easy when only general principles receive consideration. Also, it is relatively simple to outline rational specifications for a grade of gasoline that under most conditions will satisfy the great majority of users. In other words, it is easy to describe in general terms the desirable limits of volatility and reasonably easy to give figures that come safely within the limits. To define the real limits instead of stating figures safely within them is, however, a totally different problem, one involving a number of factors that can not be disregarded. In general,

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however, it may be said that the upper limit of volatility is fixed by average present-day motor construction.

The low limit, or rather the percentage of constituents volatile enough to insure ready starting of a motor, varies with the design of the engine, and also with existing temperature conditions. It is obvious that to "start" satisfactorily, gasoline must contain more low-boiling constituents in the winter than in the summer, and more in cold climates than in mild. All of these considerations emphasize the impossibility of fixing temperature limits that will in all cases economically and satisfactorily define the product "gasoline." In general usage "gasoline" is thought of as something that will start an automobile engine and keep it going when started. The "goodness" of the gasoline from the point of view of the average user depends largely on ease of starting and only in a minor way on the possible mileage per gallon or on freedom from carbon deposition.

DISTILLATION METHODS.

The distillation methods now generally used in the laboratories of refiners vary in some details, but are mostly modifications of the Engler-Ubbelohde method. This method has various basic deficiencies and is inadequate for the analysis of crude oil, as has been shown by some recent experiments of the Bureau of Mines.[a] It is possible that a modification of the Hempel method, employed by the bureau for this work and also for a recent study[b] of the properties of gasoline, might be more satisfactory for general testing purposes. However, the Engler-Ubbelohde methods are so widely employed that they seem as little likely to be abandoned as the Baumé gravity scale. For examining gasoline the method is more nearly adequate than for examining crude oil, because all that is necessary is a uniform basis of comparison for different gasolines.

The use of the various modifications is determined chiefly by the amount of information sought. In some laboratories it is customary to determine only the initial boiling point and the "end" or "dry point," the latter being the highest temperature registered by the thermometer at the end of the distillation. The initial boiling point is variously taken, but generally as the temperature read when the first or the fifth drop falls from the end of the condenser.

Sometimes analyses are more elaborate and the temperature is read for each 5 or 10 per cent distilled and, if desired, the gravities of the various fractions are determined.

[a] Rittman, W. F., and Dean, E. W., The analytical distillation of petroleum; Bull. 125, Bureau of Mines, 1916, pp. 1–75; Jour. Ind. and Eng. Chem., vol. 7, 1915, pp. 185–195, 754–760.

[b] Rittman, W. F., Jacobs, W. A., and Dean, E. W., work cited.

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Laboratory practice differs in respect to the size of the distilling flask and the quantity of gasoline taken as an original charge. The original Engler flask was designed to hold 100 c. c. of oil. When only initial boiling-point and end-point determinations are to be made this size is generally used. However, there are certain disadvantages from the use of so small a quantity. When percentage cuts are to be made many laboratories use larger flasks of such dimensions as to give about the same proportionate degree of fractionation as is attained by the original 100 c. c. flask. Charges of 200 c. c. and of either 400 or 500 c. c. are often distilled, the latter being taken when the specific gravities of small fractions are to be measured with hydrometers.

In formulating specifications the conditions of distillation must be exactly defined in order to permit equitable settlement of disputes. It is probable, however, that for the distillation of gasoline the results of all of the open-flask methods agree pretty closely and it is by no means necessary for the testing laboratories of refineries to discard present methods unless products approach permissible limits very closely.

The advantages in using the various sizes of charges are more or less evenly balanced. The use of 400 or 500 c. c. is probably most convenient when it is desirable to measure the gravities of fractions. The Bureau of Mines has in the past favored 200 c. c. for its own experiments, because the volume of the distillates permitted gravity measurements with the Westphal balance, which has been employed instead of the hydrometer.

In the present analytical methods for gasoline it has not seemed necessary either to separate fractions or to measure gravities. Hence one of the chief advantages resulting from the use of large original charges vanished. There remain certain mechanical advantages, particularly as regards minimization of experimental error, but it finally seemed that for the needs of the present work the 100 c. c. charge is most desirable.

The sample of gasoline to be examined can be shipped in the convenient 4-ounce sample bottle which is in common use in the petroleum industry. In addition, an experiment can be made quickly, and the results are accurate enough for general purposes. The chief advantage, however, is that the method is already so standardized that it is not an innovation.

The American Society for Testing Materials has had occasion to adopt a distillation method for the petroleum products used as turpentine substitutes, and this method, with one or two minor modifications, seems highly desirable for use with gasoline. The apparatus is standard and can be readily purchased; the details of manipulation are simple and yield satisfactory results. The method

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and apparatus are described in detail on a later page, but a general description seems desirable here. The method involves the use of a thermometer of standard dimensions, a standard 100-c. c. Engler flask, and an ice-cooled metal condenser tube set at an angle of 75° from the perpendicular. The gasoline is distilled at a standard rate of 4 to 5 c. c. a minute, temperature readings being made as each 10 per cent has distilled and when the end or dry point is reached. The latter is the highest temperature read on the thermometer after the flask boils dry.

It has been customary in the past to read as the initial point the temperature at which the first drop falls. This point is difficult to measure accurately, and there seems to be no advantage in using it instead of the more convenient 10 or 20 per cent mark. It seems that the gasoline should be defined by four points, which may conveniently be the 20 per cent mark, the 50 per cent mark, the 90 per cent mark, and the dry point. Some controversy has arisen as to the desirability of a 90 per cent temperature instead of the 95 per cent temperature. The former has the advantage of greater ease of accurate determination. The latter is preferred by some chemists, seemingly on general principles, without very definitely founded evidence. It is thought that by using the 90 per cent temperature and the dry point all needs are met, and experimental difficulties are avoided.

Satisfactory figures for these points insure the following desirable qualities of a gasoline:

(*a*) Enough moderately low-boiling constituents to permit easy starting of a motor;

(*b*) Not enough low-boiling constituents to cause undue tendency toward evaporation losses;

(*c*) Fairly uniform boiling range and not too great a percentage of constituents boiling at higher temperatures;

(*d*) Only a very small percentage of constituents of very high-boiling point. In other words, not too high an end point.

Requirement *b*, which is satisfied by placing the lower limit for the 20 per cent mark, is introduced for the purpose of making a gasoline reasonably safe and free from evaporation losses. It is a limit that is not likely to be overstepped, on account of commercial conditions.

REVIEW OF THE GASOLINE SITUATION.

Before a system of actual specifications is discussed it seems desirable to summarize the status of the gasoline market at present (April, 1917). During the last year or two the total production of refinable crude oil has not increased, although the demand for gaso-

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line has grown tremendously. That the supply of gasoline has kept pace with the demand has been due chiefly to the use as motor fuel of a greater proportion of the crude oil produced. Cracking processes have helped to increase the supply, and the extraction of gasoline from natural gas had contributed considerably. In addition, many refiners have augmented their production by what may be called "cutting deeper into the crude." Some of the fractions of petroleum that were formerly marketed under other names and for other purposes are now sold as gasoline, thus in effect increasing the production of this commodity.

Among automobile users there is a more or less prevalent feeling that producers and marketers are taking advantage of them. This feeling is due in part to higher prices and in part to changes in the composition of the motor fuel. An added source of discontent is the fact that some filling stations are believed to deliver to their customers a product made by blending gasoline with varying proportions of kerosene. As a result of this situation it is possible that local or State legislative bodies may enact laws for standardizing the product sold as gasoline and for preventing fraud through its adulteration with kerosene.

Faulty legislation will probably be as much to the disadvantage of the consumer as of the producer, especially if it prevents the marketing of products that fail to meet definite numerical standards. On the other hand, there seems to be no inherent reason why the consumer should not know what he is buying, and in view of the present situation it would seem good business policy for the marketers to supply the information that is desired. Users wish to have assurance that they are not being cheated, and it does not seem reasonable to suppose producers and marketers are unable to give this assurance. However, the function of the Bureau of Mines is not to solve this problem, which really falls in the realm of business management, and the present paper is limited to the purpose of supplying technical information.

At present (April, 1917) the grade of gasoline generally marketed in California seems to be considerably lower in distillation range than that generally sold in other parts of the country. In the Mid-Continent field the products vary from a grade approximately equivalent to that sold on the Pacific coast to products of relatively high "end point." Many of these high "end-point" products are so carefully produced and marketed that they are used with perfect satisfaction. On the other hand, the bureau has evidence that, in limited degree at least, gasoline has been sold that was improperly refined or was blended with burning oil by the marketer. Such gasoline naturally has not given as general satisfaction as the "fool proof" light gasoline or the scientifically blended heavy motor fuel.

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In the East the general output of motor fuel has a moderately high end point, but is probably, though not certainly, a little lighter than could be used with general satisfaction under favorable engine conditions.

GASOLINE SPECIFICATIONS.

In a way, the present problem has grown from the bureau's task of preparing specifications for Federal purchases of gasoline in the District of Columbia. The method adopted in preparing these specifications was briefly as follows: Samples of the various types of motor gasolines sold in the District were analyzed. A specification was then written which represented the average product already on the market, previous experiences having indicated this to be satisfactory. The procedure adopted did not concern the problem of exactly what properties a gasoline might have and be satisfactory, but simply made it possible for the Federal departments to obtain motor fuel suitable for the motors in use and equal in quality to that dispensed to private users.

Specifications for several other naphthas and gasolines required for special purposes were written in a similar way, necessary information being obtained from the analyses of readily obtainable products that had been proven satisfactory for the particular uses.

This method of determining specifications is not absolutely scientific, but is recommended as being highly practical. If any community, organization, or firm desires to purchase gasoline on specification it should first ascertain what products it can buy at standard prices and then find out which of these are satisfactory in use. Information regarding these two points needs to be supplemented only by satisfactory analytical methods which, it is thought, will be generally available on the basis of the information presented in this paper.

LIMITS AND REQUIREMENTS OF GASOLINE SPECIFICATIONS.

An ideal system of specifications would, by a minimum of simple requirements, eliminate all unsatisfactory products without discriminating against any that are desirable. This ideal is, of course, impossible of attainment for gasoline, partly because no hard and fast line differentiates good gasoline from bad, and partly because a satisfactorily simple specification can not cover all possible sources of discrepancy. In general, however, the tests discussed later furnish an adequate index of quality for the normal products marketed as gasoline, and will probably be satisfactory until such time as new and unforeseen developments occur in the refining industry.

The requirements which are considered adequate for the present are color, freedom from acidity, and volatility. Color in itself is

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of minor importance but generally, though not infallibly, indicates whether a gasoline is properly refined. At present producers show little tendency to market gasolines that do not meet requirements in this respect. The requirement of freedom from acid is important, and the simple test should always be made, even though the almost universal care taken by refiners has made it practically unnecessary.

In discussing volatility requirements it has been deemed inadvisable to state definite figures, as it is possible that undue importance may be attached to the limits mentioned. The bureau has written specifications for Federal purchases of gasoline, but does not wish to give undue prominence to these figures which deal with products used under more or less definitely known weather conditions and in the motors owned and operated by the Government departments.

Only one definite temperature limit is stated, that which prevents a gasoline from having too high a proportion of volatile constituents. This limit is one which for commercial conditions is not likely to be passed, but it is included to make possible the rejection of gasoline that obviously is unfit to store or handle. Other temperature limits are left indeterminate or else given in relative terms.

The two limits upon which most emphasis is laid are the temperatures below which 20 per cent and 90 per cent of the gasoline distill. Any two other percentage marks near the initial and the upper end of the distillation range might serve, but these two points are the most satisfactory for determination by the analyst, and it is thought are at least as important as any others with regard to the behavior of the gasoline in the motor. A tolerance is allowed for each limit, on the assumption that a moderate discrepancy in one does no harm if the other is at least an equal amount below the required mark. However, the compensation is limited to variations not exceeding 10° C. (18° F.). Thus, for example, it is assumed that gasolines having the following distillation limits are of approximately equivalent utility as motor fuel:

Hypothetical gasolines of approximately equal value as motor fuel.

Hypothetical sample No	1	2	3
Lower temperature limit, °C	100	110	90
Upper temperature limit, °C	180	170	190

As this compensating effect has not been thoroughly studied it seems desirable to limit the tolerance to variations not greater than the amount stated above.

A limit for the 50 per cent mark is fixed not because it will ordinarily be of significance, but because it will tend to prevent the marketing of "freak" naphthas that might prove unsatisfactory. The requirement that the "dry point," or highest temperature read on the thermometer after the distilling flask goes dry, shall not exceed the

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90 per cent temperature by more than 55° C. (99° F.) is liberal, but is sufficient to discriminate against improperly distilled gasolines and unsatisfactory blends of gasoline and kerosene.

A lower limit of 70° C. (158° F.) is placed on the 20 per cent mark, this also being of importance only with possible "freak" gasolines. It is, however, a limitation that has a sound and practical basis, as such gasolines are subject to serious evaporation losses.

PROPOSED SPECIFICATIONS FOR MOTOR GASOLINE.

COLOR.

Requirement.—Water white.

Method of determination.—Inspection of column in 4-ounce sample bottle.

ACIDITY.

Requirement.—Total absence.

Method of determination.—Ten c. c. of the gasoline is to be shaken thoroughly with 5 c. c. of distilled water. The aqueous extract must not color blue litmus paper pink.

VOLATILITY.

Requirements.—The gasoline shall, when distilled by the method described hereafter, meet the following requirements:

(*a*) The temperature read on the thermometer when 20 per cent has distilled shall not be below 70° C. (158° F.) nor above whatever limit is fixed after due consideration of conditions of use.

(*b*) The temperature read when 90 per cent has distilled shall not be above another limit similarly chosen.

(*c*) The temperature read when 50 per cent has distilled shall not be higher than a mark half way between the 20 per cent and the 90 per cent limit.

(*d*) The dry point shall not exceed the actual 90 per cent reading by more than 55° C. (99° F.).

Tolerance.—If either the 20 per cent or the 90 per cent temperature mark is above the required limit by an amount not exceeding 10° C. (18° F.), the gasoline may be considered acceptable if the sum of the two temperatures read for the 20 and the 90 per cent marks do not exceed the sum of the adopted limits.

DISTILLATION METHOD AND APPARATUS.

The distillation method prescribed is approximately that recommended by Subcommittee XI of Committee D_1 of the American Society of Testing Materials.[a]

[a] Am. Soc. Test. Mat. Year Book for 1915, pp. 568–569, Part I, Committee Reports, 1916, vol. 16, pp. 518–521.

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The two noticeable points of variation are the method of reading temperatures against fixed percentage points and the use of a thermometer of lower range. The method of the American Society for Testing Materials is proposed for the analyses of turpentine substitutes, which are petroleum products of higher boiling range than gasolines.

The apparatus used in the distillation should be as follows (see Plate I):

FLASK.

The flask used shall be the standard 100 c. c. Engler flask, described in the various textbooks on petroleum. The dimensions are as follows:

Dimensions of flask.

Dimensions.	Cm.	Inches.
Diameter of bulb	6.5	2.56
Diameter of neck	1.6	0.63
Length of neck	15.0	5.91
Length of vapor tube	10.0	3.94
Diameter of vapor tube	0.6	0.24

Position of vapor tube, 9 cm. (3.55 inches) above surface of oil when the flask contains its charge of 100 c. c. The tube is approximately in the middle of the neck.

The flask shall be supported on a ring of asbestos having a circular opening 1¼ inches in diameter; this means that only this limited portion of the flask is to be heated. The use of a sand bath is not approved.

CONDENSER.

The condenser shall consist of a thin-walled tube of metal (brass or copper), ½ inch internal diameter and 22 inches long. It shall be set at an angle of 75° from the perpendicular and shall be surrounded with a water jacket of the trough type. The lower end of the condenser shall be cut off at an acute angle and shall be curved down for a length of 3 inches. The condenser jacket shall be 15 inches long.

THERMOMETER.

The accuracy of distillation primarily depends on the accuracy of the thermometer and on this account the instrument should be so defined that the results of different analysts may check. The thermometer described in the report of the American Society for Testing Materials is not adapted for use with gasoline, its range being unnecessarily high and the lower temperatures being difficult to read because of interference from the cork in the neck of the distillation flask.

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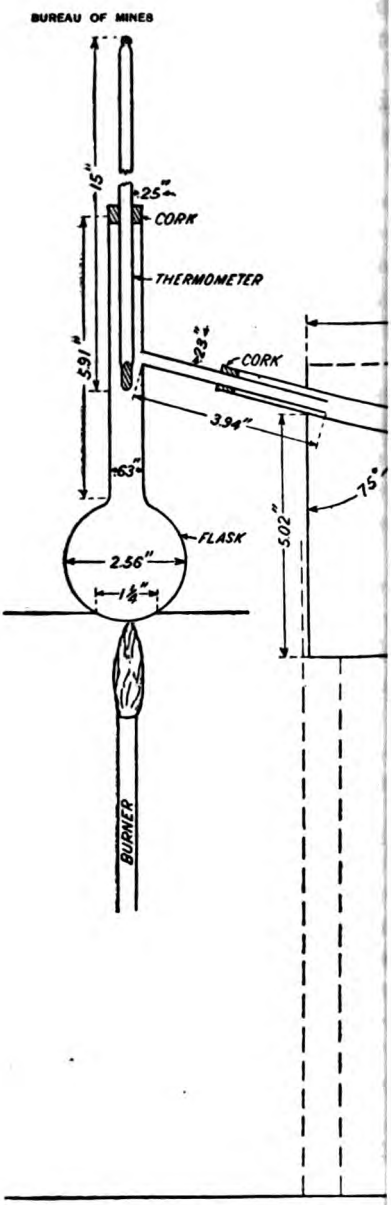

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The present discussion does not deal with the details of temperature measurement but simply indicates requirements that should be met and will insure that the maximum possible variations in thermometer readings at different analytical laboratories can not exceed 1° or 2° C.

Briefly, the thermometer should be an accurate "nitrogen-filled" instrument with a short bulb (length 10 to 15 mm., 0.39 to 0.59 inch) and with the mark for 35° C. (95° F.) at a distance between 100 and 120 mm. (3.94 to 4.73 inches) from the top of the bulb. The thermometer should be scaled for total immersion.

The above requirements insure that almost always the lowest temperatures registered may be read above the cork of the distillation flask, and variations because of the so-called "stem correction" will always be practically the same. The stem correction should not be applied, but it should be understood that results of distillations are expressed in terms of thermometer readings, not of actual temperatures. The use of partial-immersion thermometers is not recommended for distillations, as these instruments are no more likely to agree with one another than are the more common total-immersion thermometers.

The following specification for a gasoline distillation thermometer is offered so that the prospective purchaser may be able to state definitely what he requires and by so doing obtain a satisfactory instrument. The specification has been submitted to several manufacturers of thermometers, who state that it insures the obtaining of a satisfactory high-grade instrument without imposing on the maker unnecessary and troublesome restrictions that increase the cost.

SPECIFICATIONS FOR GASOLINE DISTILLATION THERMOMETER.

The thermometer should be made of selected enamel-backed tubing, having a diameter between 5.5 and 7 mm. The bulb should be of Jena normal or Corning normal glass; its diameter shall be less than that of the stem and its length between 10 and 15 mm. The total length of the thermometer should be approximately 380 mm. The range should cover 0° to 270° C., with the length of the graduated portion between the limits of 210 and 250 mm. The point marking a temperature of 35° C. should be not less than 100 nor more than 120 mm. from the top of the bulb.

The scale should be graduated for total immersion. The accuracy must be within about 0.5° C.[a] The space above the meniscus must be filled with an inert gas; such as nitrogen, and the stem and bulb must be thoroughly aged and annealed before being graduated.

[a] If desired, a Fahrenheit thermometer may be obtained on these specifications by substituting Fahrenheit equivalents for the several Centigrade marks.

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All material and workmanship must be of the best. The scale shall be marked for single-degree intervals. Each tenth degree shall be numbered and each fifth degree distinguished by a longer mark.

METHOD OF DISTILLATION.

The flask connected with the condenser shall be filled with a 100-c. c. charge of gasoline, which shall be measured from a 100-c. c. graduated cylinder. The same cylinder may be used without drying as the receiving vessel for the distillate. Heat shall be applied to the flask in regulated degree, care being taken that the whole distillation from beginning to end shall proceed at a rate of not less than 4 nor more than 5 c. c. a minute. Readings of the thermometer shall be made as each 10 per cent distills.

The dry point or highest temperature reading at the end of the distillation shall also be recorded. The distillation loss shall be determined by adding the percentage of residue in the distilling flask, after cooling, to the percentage of total distillates held in the receiver. If the distillation loss is over 3 per cent, a check distillation shall be made, as excessive loss may indicate that the rate of distillation at the beginning was too rapid. In case the magnitude of the loss is confirmed this fact is of importance in indicating that the gasoline contains very volatile constituents, particularly those derived from added casing-head gasoline.

The condenser trough shall be filled with a mixture of cracked ice and water (not dry cracked ice), and during the distillation sufficient ice shall be kept in the trough to prevent the temperature of the cooling water exceeding 8° C. (46° F.).

If distillations are made at high altitudes or when barometric pressures are low, allowances may be made for this factor. In general, recording the barometric pressure read at the time of the distillation will suffice and it is recommended that whenever there is possibility of dispute over the results of a distillation this should be done.

The thermometer bulb should be covered with a thin film of absorbent cotton; this keeps the glass always wet with the condensate from the vapor and thus prevents possible fluctuations in the temperature. It also tends to prevent superheating of the bulb at the end of the distillation and thus makes possible an accurate determination of the dry point.

The whole procedure is relatively simple but involves certain details of manipulation of more or less importance. The use of apparatus at least approximately as described is essential, although the method is such that no considerable discrepancies will result if the apparatus is not exactly standard. The chief source of difficulty is the rate of heating. It is of course desirable to bring the initial

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charge up to the boiling point as rapidly as possible in order not to waste time, but unless care is taken the distillation will start too rapidly and there will be losses in the form of uncondensed vapor. In consequence the actual percentages will be higher than those read and the temperatures may likewise be noticeably high. If, however, the distillation loss is not permitted to exceed the stated amount this difficulty can be avoided. In case the gasoline to be tested contains considerable proportions of constituents difficult to condense, the condenser trough may be filled with a freezing mixture and the receiver also kept cooled. If this is done, it is desirable to measure out the original charge at the temperature of this freezing mixture in order to avoid discrepancies due to changes of volume with temperature.

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CENTIGRADE SCALE COMPARED WITH FAHRENHEIT.

Equivalent temperature degrees on the Centigrade and the Fahrenheit scale are shown in the table below:

TABLE 1.—*Centigrade scale compared with Fahrenheit.*

Range, 30° C. (86° F.) to 309° C. (588° F.).

°C.	0	1	2	3	4	5	6	7	8	9
3.....	86	88	90	91	93	95	97	99	100	102
4.....	104	106	108	109	111	113	115	117	118	120
5.....	122	124	126	127	129	131	133	135	136	138
6.....	140	142	144	145	147	149	151	153	154	156
7.....	158	160	162	163	165	167	169	171	172	174
8.....	176	178	180	181	183	185	187	189	190	192
9.....	194	196	198	199	201	203	205	207	208	210
10....	212	214	216	217	219	221	223	225	226	228
11....	230	232	234	235	237	239	241	243	244	246
12....	248	250	252	253	255	257	259	261	262	264
13....	266	268	270	271	273	276	277	279	280	282
14....	284	286	288	289	291	293	295	297	298	300
15....	302	304	306	307	309	311	313	315	316	318
16....	320	322	324	325	327	329	331	333	334	336
17....	338	340	342	343	345	347	349	351	352	354
18....	356	358	360	361	363	365	367	369	370	372
19....	374	376	378	379	381	383	385	387	388	390
20....	392	394	396	397	399	401	403	405	406	408
21....	410	412	414	415	417	419	421	423	424	426
22....	428	430	432	433	435	437	439	441	442	444
23....	446	448	450	451	453	455	457	459	460	462
24....	464	466	468	469	471	473	475	477	478	480
25....	482	484	486	487	489	491	493	495	496	498
26....	500	502	504	505	507	509	511	513	514	516
27....	518	520	522	523	525	527	529	531	532	534
28....	536	538	540	541	543	545	547	549	550	552
29....	554	556	558	559	561	563	565	567	568	570
30....	572	574	576	577	579	581	583	585	586	588

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